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This is the fourth report from this Source and further exploita-
tion is being conducted. Requests for further information can
be accepted.

1. Introduction

This report covers my work on the following catalysts:

- a. Oil Cracking Catalyst
- b. Hydroforming Catalyst
- c. Dehydration Catalyst for Butylene Production
- d. Hydrogenation Catalyst for Cyclohexanol Production
- e. Hydrogenation Catalyst for Hexanediol - 1,6 Production
- f. Hydrogenation Catalyst for Isobutyl Dichloride Preparation
- g. Dehydration Catalyst for Isoprene Production
- h. Dehydration Catalyst for Adipic Dinitrile Production
- i. Dehydration Catalyst for Toluene Production

a. Oil Cracking Catalyst

- (1) The standard Leuna oil cracking catalyst was an alumina silica catalyst, similar to the Houdry oil cracking catalyst. Its chemical composition was $1Al_2O_3 \cdot 9 SiO_2$ which was just outside the range of the Houdry patent. This patent was disregarded during the war, and the silica content was increased to $1Al_2O_3 \cdot 10 SiO_2$.

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- (2) The catalyst was prepared in three steps, each at a different plant. Active silica, or kieselgel, was produced at Osterode in a plant of 8 - 10 metric tons/month capacity. The required active alumina was prepared at Leuna. The Kieselgel and active alumina were combined at Schkeelen, near Osterfeldt, to produce the finished catalyst.
- (3) The kieselgel was prepared as follows: Sodium silicate solution, of 1.333 specific gravity, was mixed with sufficient 2 normal sulfuric acid to provide a pH of 3.5 at a temperature not exceeding 15°C, after which, by heating to 60 - 70°C, a gel was formed. This gel was crumbled, washed by decantation, dried at 120 - 150°C, and ground in a ball mill to produce a white powder of active silica or kieselgel. Ammonia vapors, encountered at any stage, would result in an inactive silica.
- (4) The active alumina was prepared as follows: A strong solution of sodium aluminate, containing about 200 gm Al_2O_3 liter, was prepared from metallic aluminum and sodium hydroxide solution, and then mixed with sufficient 20% nitric acid to provide a pH of 5.5 - 6.5 at a temperature not exceeding 40°C. The gelatinous precipitate of aluminum hydroxide, thus formed, was filtered and washed in a filter press, dried at 120 - 180°C, and ground in a ball mill to produce a white powder of active alumina. It was found that if the active alumina were peptized, by the addition of about 2% of the nitric acid theoretically required to convert all the alumina to aluminum nitrate, the strength and activity of the finished catalyst would be increased.
- (5) At Schkeelen the active alumina could be first peptized, or else kneaded directly, for 1 - 2 hours, with kieselgel and water. The resulting dough was extruded into 6 mm diameter rods, which were formed, in a special machine, into spheres of 6 mm diameter. After drying at 120°C, these spheres were heated at 450°C, for 2 hours, in order to obtain the desired mechanical properties, and to assure denitration if the alumina had been peptized.
- (6) The 6 mm diameter spheres of oil cracking catalyst were white, porous, hard, and yet could be bounced from the floor to the ceiling without fracture. This elastic behavior was one reason for mechanical stability. The catalyst had a long life, both as regards mechanical strength and catalytic activity. When replaced after six months, it was still strong and quite active.
- (7) Because of these excellent properties it was planned, as early as 1941, to erect a moving bed or Thermoform catalytic cracking plant in Pressburg (Bratislava), Czechoslovakia. A pilot plant with fixed bed was erected south of Leuna, near Deuben, but never put into operation because sufficient catalyst was not available.

- (8) [REDACTED] at Osterode to assist Dr Kula, who was in charge of the plant. At that time the activity of the oil cracking catalyst had sadly deteriorated. The cause was finally traced to the Leuna produced alumina, which although still active enough for use in hydroforming and dehydration catalyst, was no longer sufficiently active for use in the oil cracking catalyst. Before the procedure could be corrected, the territory was occupied by the Allies in May 1945.

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- (9) I have no knowledge of the erratic production of the oil cracking catalyst plant. The catalyst worked well with the middle petroleum fraction from Zistersdorf, Austria, which was used in the laboratory unit.

b. Hydroforming Catalyst

- (1) The catalyst developed at Leuna for the dehydrogenation and conversion of paraffinic hydrocarbons into cyclic and aromatic hydrocarbons in the presence of hydrogen was composed by weight of 90% Al_2O_3 , 10% MoO_3 . It was prepared on a laboratory scale by mixing purified alumina with a solution containing molybdic oxide dissolved in 25% ammonia solution, then evaporating, oven drying at 120 - 180°C, grinding, and pelleting to 9 x 9 mm cylinders. On a large scale it was prepared by spraying the ammonium molybdate solution on 9 x 9 mm cylinders of purified alumina in an agglomeration drum, followed by drying at 120-180°C. It was used in a fixed-bed, full-scale plant, started up in 1942, in Moosbierbaum, Austria, where Rumanian oil was hydrofermed at 15 atm to produce basic stock for aviation fuels.
- (2) I do not know production figures for catalyst or oil plants.

c. Dehydrogenation Catalyst for Butylene Production

- (1) The Leuna dehydrogenation catalyst for the production of both normal and isobutylene was composed by weight of 90% Al_2O_3 , 8% Cr_2O_3 , and 2% K_2O . It was prepared by treating alumina with a concentrated solution of chromic acid - potassium dichromate, followed by drying at 120 - 180°C, grinding, and pressing into 6 x 6 mm cylinders.
- (2) This catalyst was produced in the catalyst plant in southern Leuna, and used in a pilot plant in northern Leuna to convert isobutane into isobutylene by simply passing isobutane through the reactor at 450 - 480°C. After every 8 hours of operation, the catalyst was regenerated by blowing with air to burn off the coke.
- (3) In late 1943, a moving-bed full-scale plant, known as the DHD plant, was erected in southern Leuna. The catalyst fell through vertical tubes of silicon chrome steel, dropping on horizontal feeler-rods, attached to small square plates, on the reactor shell. The workman, by extending a small rod, or even a pencil, from the square plate to his ear, could hear whether or not that particular tube was operating properly. The tubes were heated by a gas-fired oven, with recycling of fire gases to control the temperature. The catalyst was discarded after 300 kg of isobutylene had been produced per kg of catalyst.
- (4) I have no production figures for catalyst plant, pilot plant, nor full-scale plant.
- (5) The integration of the isobutylene plant was as follows: Normal butane, probably obtained by the hydrogenation of coal using tungsten oxide on clay or fuller's earth as catalyst was isomerized at Leuna to isobutane using aluminum chloride catalyst. Isobutylene, prepared by isobutane dehydrogenation as described above, was polymerized by sulfuric acid catalyst to form isooctene. This was hydrogenated over nickel catalyst to form isooctane, which was blended with basic stock to produce aviation fuels. Later by the alkylation process with a sulfuric acid catalyst, isooctane could be formed in one direct step by the reaction of isobutane and isobutylene.

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d. Hydrogenation Catalyst for Cyclohexanol Production

- (1) The standard Leuna hydrogenation catalyst had the formula composition $3\text{Ni} \cdot \text{Al}_2\text{O}_3$, and was prepared as follows: nickel was digested with nitric acid, and aluminum with caustic soda, and the resulting solutions of nickel nitrate and sodium aluminate coprecipitated at a pH of 5.5 - 6.5 at a temperature not exceeding 40°C to form mixed nickel hydroxide and aluminum hydroxide, which after filtration and washing in a filter press was dried at 180°C , ground in a ball mill, and pressed into 6 x 6 mm or 9 x 9 mm cylinders. The catalyst at this stage was given the Leuna No 3390.
- (2) These cylinders were then heated to 400°C while exposed to a stream of nitrogen, which was gradually replaced by hydrogen, and after an 8-hour exposure to hydrogen, at 400°C , using 1,000 volumes of hydrogen per hour per volume of catalyst, the catalyst was cooled to room temperature, maintaining a steady stream of hydrogen. If exposed to air at this stage it would be completely deactivated. However, by replacing the hydrogen first by a stream of nitrogen, and then by air, only a small and controlled amount of deactivation would result from the 0.2 - 0.5% of oxygen contained in the commercial nitrogen. This catalyst, Leuna No 6523, could then be reactivated in the reactor before use, by heating in a stream of hydrogen.
- (3) This catalyst was used for the hydrogenation of phenol to cyclohexanol, which could then be oxidized with nitric acid to form adipic acid, an intermediate in the manufacture of nylon. It was also used at Leuna as a catalyst for the production of heavy water by isotope exchange at normal pressure.
- (4) It is now being produced at Leuna at a rate of about 10 metric tons per month. I do not know for what purpose since cyclohexanol is no longer produced at Leuna. Perhaps it is being sold.

e. Hydrogenation Catalyst for Hexanediol - 1,6 Production

- (1) This catalyst was a copper - barium - chromite Homer Adkins catalyst. It was prepared by mixing a solution of copper nitrate and barium nitrate with a solution of ammonium dichromate to form a precipitate which was washed and dried. It was then heated to 250°C at which temperature the brown precipitate spontaneously ignited to produce a black powder in which the chromate had been reduced to chromite. This powder could be activated only by 10% acetic acid. Following washing and drying, the powder was formed into finished 6 x 6 mm cylinders.
- (2) This catalyst was used to hydrogenate the ethyl ester of adipic acid to form hexanediol - 1,6 with ethanol and water by-products. The hexanediol - 1,6 may be used as a dihydroxy alcohol for reaction with fatty acids to produce lacquers like the alkydals, or it may be used to produce esters which serve as lubricating oils.
- (3) In 1941-42 a pilot plant was in operation in northern Leuna, in Bldg 219. It produced about 5 - 7 kg per week of catalyst.

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f. Hydrogenation Catalyst for Isobutyl Dichloride Preparation

- (1) This catalyst was a pure nickel catalyst, made at the request of Dr Striegler, now in Dzershinsk. It was prepared from basic nickel carbonate which was dried, roasted to a black powder, pressed into 6 x 6 mm cylinders, and reduced with hydrogen at 280°C for 36 hours. It was stored in toluene to prevent deactivation with air.
- (2) This catalyst was used for the hydrogenation of isobutylene dichloride to isobutyl dichloride. A low operating temperature about 100°C was required so as not to displace the chlorine

for hydrogenation of ethylene to ethane at temperatures as low as -80°C.

g. Dehydration Catalyst for Isoprene Production

- (1) This catalyst was composed of about 50% kieselguhr, the remainder being alumina and phosphoric acid in proportions I do not recall. It was prepared by mechanically mixing and kneading the constituents to form a dough which was extruded into 6 mm diameter rods and roasted for one hour at 400 - 500°C. The final product was brittle and could be broken to desired lengths.
- (2) This catalyst was used in a pilot plant at Leuna for the production of isoprene from isobutylene and formaldehyde by a two-stage process. The isobutylene and formaldehyde were first reacted at room temperature in the presence of 20% sulfuric acid to form a substituted dioxane intermediate. This intermediate, in the presence of the dehydration catalyst above, split and was dehydrated to form isoprene and water. A total of about 30 tons of isoprene was produced and sent to Schkopau.
- (3) The process worked well and was the subject of a patent.

h. Dehydration Catalyst for Adipic Dinitrile Production

- (1) In the early stages of this work, boryl phosphate was used as a catalyst. Later it was found that a catalyst of 50% kaolin and 50% tungsten oxide was better. This latter catalyst was prepared by mixing the constituents with water or dilute ammonia solution in a ball mill, to produce a thick slurry, like wet plaster, which was evaporated, dried at about 120°C, and pressed into 6 x 6 mm cylinders. If the kaolin had first been heated at 600°C for 2 hours, before mixing, an improvement in catalytic activity was obtained.
- (2) This catalyst was used to produce adipic dinitrile by reaction of adipic acid and ammonia. Dr Dierichs, now at Leverkusen, worked on this process. By hydrogenation over Raney cobalt catalyst, the product could be converted into hexamethylene diamine, an intermediate for nylon production.
- (3) A pilot plant, which later served as a small full-scale plant, was located in northern Leuna. Its capacity was about 30 metric tons per month.

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1. Dehydration Catalyst for Toluene Production

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nesium oxide, It was prepared by mixing and kneading the above constituents, followed by drying on an aluminum sheet at 120 - 150°C. The aluminum reacted with the phosphoric acid, producing hydrogen, which resulted in an active and porous catalyst, gray in color and irregular in size.

- (2) This catalyst was prepared in a full-scale catalyst plant in southern Leuna. It was used in 25X1A full-scale production plant at Waldenburg, Silesia, where toluene was prepared by the dehydration reaction of methanol with benzene, according to the Witol process. Dr Marcus, now in Buenos Aires, was interested in this process. Unfortunately, the catalyst caked during operation, and air compressors were often required to remove it. As a result, the process was very expensive.
- (3) The plant at Waldenburg had a capacity of 4,000 metric tons per month of toluene, but is no longer producing.

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